

Toward the Description of van der Waals Interactions within Density Functional Theory

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ABSTRACT: On the basis of the adiabatic connection formula we propose several approximations for the total correlation energy functional, which, in the limit of two separated neutral subsystems, correctly reproduce the van der Waals R^{-6} behavior. We have calculated the corresponding van der Waals coefficients as well as *total* correlation energies, thus demonstrating the feasibility of a “seamless” functional. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 12–22, 1999

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Introduction

For many years, density functional theory (DFT)^{1–4} has been successfully employed to describe the electronic structure of atoms, molecules, and solids. Recently, DFT has become increasingly popular in theoretical chemistry due to the continuing improvement of the exchange-correlation (xc) functionals available.

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DFT yields accurate total energies of atoms and molecules. However, none of the commonly used functionals contains the van der Waals (vdW) interaction. This means that they do not reproduce the well-known R^{-6} behavior characterizing the interaction of two widely separated neutral fragments. Clearly, the true correlation energy functional must include the vdW interaction.⁵ The conventional local density approximation (LDA) and generalized gradient approximations (GGA) are essentially local; that is, the exchange-correlation potential, $v_{xc}(\mathbf{r})$, at a point \mathbf{r} is determined by the density and its low-order gradients at the very

same point \mathbf{r} . The description of long-range forces such as the vdW interaction requires fully nonlocal functionals.

There have been several suggestions for constructing density functionals yielding the vdW interaction.^{6–10} But, until now, there is no functional that has proven to yield *both* vdW coefficients *and* total correlation energies of atoms and molecules with reasonable accuracy.¹¹ The goal of this work is to find a nonlocal xc functional which makes exactly that possible. We note that Dobson and Wang have done “seamless” calculations based on the concepts described in ref. 9 for a jellium slab situation,¹² but so far not for atoms and molecules.

In the following section we first introduce the basic concepts leading to the construction of our vdW functional. It uses results of time-dependent DFT and linear-response theory. In the subsequent sections we present several approximations along with numerical results for vdW coefficients and correlation energies.

Method

DENSITY FUNCTIONAL THEORY

We are interested in N -electron systems described by the Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V} + \hat{W} \quad (1)$$

Here, the operators \hat{T} , \hat{V} , and \hat{W} represent the kinetic energy, the external potential, and the Coulomb interaction between electrons:

$$\hat{T} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) \quad (2)$$

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i) \quad (3)$$

and

$$\hat{W} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4)$$

The formal foundation of DFT is the Hohenberg–Kohn (HK) theorem.¹ Its most important aspect is the one-to-one mapping between the external potential, $v(\mathbf{r})$, and the ground-state density, $n(\mathbf{r})$. Thus, it allows us to express formally any observable of the system as a functional of the ground-state density.

The particular form of the particle–particle interaction does not enter the proof of the HK theorem. Hence, for a noninteracting system the theorem holds as well. In spin DFT, one uses the spin densities n_\uparrow and n_\downarrow as the basic quantities; that is, all observables are understood as functionals of the spin densities. Then, by applying the HK theorem to noninteracting particles there is a uniquely determined spin-dependent single-particle potential, $v_{s\sigma}(\mathbf{r})$, that reproduces a given set of ground-state spin densities, $n_\sigma(\mathbf{r})$. From the solutions of the single-particle Schrödinger equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{s\sigma}(\mathbf{r}) \right] \varphi_{j\sigma}(\mathbf{r}) = \epsilon_{j\sigma} \varphi_{j\sigma}(\mathbf{r}) \quad (5)$$

we can compute the spin densities and the total density:

$$n_\sigma(\mathbf{r}) = \sum_j f_{j\sigma} |\varphi_{j\sigma}(\mathbf{r})|^2 \quad (6)$$

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \quad (7)$$

where $f_{j\sigma}$ is the occupation number of the orbital, $\varphi_{j\sigma}$ (either 0 or 1).

Next, we define the exchange–correlation energy, E_{xc} , by splitting the total energy of the interacting system into:

$$\begin{aligned} E_v[n_\uparrow, n_\downarrow] &= T_s[n_\uparrow, n_\downarrow] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \\ &+ \frac{e^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ E_{xc}[n_\uparrow, n_\downarrow] \end{aligned} \quad (8)$$

where T_s denotes the kinetic energy of the noninteracting system. Applying the HK variational principle to this representation of the total energy one finds that the single-particle potential, $v_{s\sigma}(\mathbf{r})$, reproducing the spin densities of the *interacting* system, the so-called Kohn–Sham (KS) potential,² is given by:

$$v_{s\sigma}(\mathbf{r}) = v(\mathbf{r}) + e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc\sigma}(\mathbf{r}) \quad (9)$$

where the xc potential, $v_{xc\sigma}(\mathbf{r})$, is the functional derivative of the xc energy:

$$v_{xc\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} \quad (10)$$

By employing an approximate functional for E_{xc} , and solving eqs. (5), (6), (7), and (9) self-con-

sistently, we find the ground-state spin densities. Then, the total energy functional [eq. (8)] yields the ground-state energy.

Because we know the exact expression for the exchange energy in terms of the KS spin orbitals:

$$E_x^{\text{KS}}[\{\varphi_{j\sigma}\}] = -\frac{e^2}{2} \sum_{\sigma} \sum_{jk} f_{j\sigma} f_{k\sigma} \int d^3r d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (11)$$

we may concentrate on finding approximate functionals for the correlation energy, defined as:

$$E_c = E_{\text{xc}} - E_x^{\text{KS}} \quad (12)$$

However, the use of the exact exchange requires the treatment of functionals depending explicitly on the KS orbitals rather than on the density. In this case, the xc potential cannot be calculated by a straightforward functional derivative, because the dependence on the density is not known explicitly. In the so-called optimized effective potential (OEP) method,^{13,14} the potential is determined by an integral equation that can be derived by applying the functional chain rule to eq. (10). In the most general case, the xc energy functional depends on all KS orbitals and KS energy eigenvalues. Then:

$$v_{\text{xc}\sigma}(\mathbf{r}) = \sum_{i\alpha\beta} \int d^3r' \left\{ \int d^3r'' \left[\frac{\delta E_{\text{xc}}[\{\varphi_{j\nu}, \epsilon_{j\nu}\}]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \right. \right. \\ \times \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{s\beta}(\mathbf{r}'')} \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})} + c.c. \left. \right] \\ \left. + \frac{\partial E_{\text{xc}}[\{\varphi_{j\nu}, \epsilon_{j\nu}\}]}{\partial \epsilon_{i\alpha}} \frac{\delta \epsilon_{i\alpha}}{\delta v_{s\beta}(\mathbf{r}'')} \frac{\delta v_{s\beta}(\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})} \right\} \quad (13)$$

leads to the OEP equation:

$$\sum_i \int d^3r' [v_{\text{xc}\sigma}(\mathbf{r}') f_{i\sigma} - u_{\text{xc}\sigma}(\mathbf{r}')] \\ \times G_{s i \sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') + c.c. \\ = \sum_i \frac{\partial E_{\text{xc}}}{\partial \epsilon_{i\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 \quad (14)$$

where:

$$u_{\text{xc}\sigma}(\mathbf{r}) = \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_{\text{xc}}[\{\varphi_{j\nu}, \epsilon_{j\nu}\}]}{\delta \varphi_{i\sigma}(\mathbf{r})} \quad (15)$$

and:

$$G_{s i \sigma}(\mathbf{r}', \mathbf{r}) = \sum_{k \neq i} \frac{\varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{k\sigma}} \quad (16)$$

The numerical solution of the OEP equation is very involved. For xc functionals depending only on the occupied orbitals, there exists a simplified scheme due to Krieger, Li, and Iafrate (KLI),^{15,16} which avoids the full numerical solution of the integral equation. Exchange-only calculations show that the KLI results are practically identical to the exact OEP results, whereas the numerical effort is comparable to conventional density functional calculations.

The above definition of the correlation energy differs slightly¹⁷ from the one used in quantum chemistry, where it refers to the difference between the exact total energy and the Hartree-Fock energy:

$$E_c^{\text{QC}} = E - E^{\text{HF}} \quad (17)$$

ADIABATIC CONNECTION FORMULA

We search for a correlation energy functional that, apart from yielding good total correlation energies, contains the vdW interaction. We start from an exact expression for E_{xc} , which is based on the so-called adiabatic connection formula (see, e.g., ref. 8):

$$E_{\text{xc}} = -\frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' w(\mathbf{r}, \mathbf{r}') \\ \times \left\{ \left[\frac{\hbar}{\pi} \int_0^\infty du \sum_{\sigma\sigma'} \chi_{\sigma\sigma'}^{(\lambda)}(\mathbf{r}, \mathbf{r}'; iu) \right] \right. \\ \left. + n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right\} \quad (18)$$

Here, $w(\mathbf{r}, \mathbf{r}') = e^2/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb interaction. $\chi_{\sigma\sigma'}^{(\lambda)}$ denotes the spin-density response function^{18,19}:

$$\chi_{\sigma\sigma'}^{(\lambda)}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta n_{\sigma}^{(\lambda)}[v_{\uparrow}, v_{\downarrow}](\mathbf{r}t)}{\delta v_{\sigma'}(\mathbf{r}'t')} \Big|_{\{v_{\uparrow}^{(\lambda)}, v_{\downarrow}^{(\lambda)}\}} \quad (19)$$

of a fictitious system with Coulomb coupling strength, λe^2 , in a potential, $v_{\sigma}^{(\lambda)}(\mathbf{r})$, which is determined by requiring that the (unperturbed) spin densities are equal to those of the fully interacting system. $n_{\sigma}^{(\lambda)}[v_{\uparrow}, v_{\downarrow}]$ denotes the spin density as a functional of the potentials, v_{\uparrow} and v_{\downarrow} , at fixed

coupling constant λ . As $\chi_{\sigma\sigma'}^{(\lambda)}(\mathbf{r}t, \mathbf{r}'t')$ depends only on the difference $(t - t')$, the Fourier transform with respect to $(t - t')$ may be taken. The resulting frequency-dependent response function, evaluated at imaginary frequencies, $i\omega$, is the one appearing in eq. (18). The integration over the coupling constant, λ , connects the fully interacting system ($\lambda = 1$) with the noninteracting KS system ($\lambda = 0$), while the (unperturbed) spin densities are held constant.

If, in eq. (18), we replace $\chi_{\sigma\sigma'}^{(\lambda)}$ by the noninteracting KS response function, $\chi_{s\sigma\sigma'}$, then we obtain the exact exchange energy, eq. (11). Consequently, the correlation energy is given by:

$$E_c = -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int d^3r d^3r' w(\mathbf{r}, \mathbf{r}') \times \int_0^\infty du \sum_{\sigma\sigma'} [\chi_{\sigma\sigma'}^{(\lambda)}(\mathbf{r}, \mathbf{r}'; iu) - \chi_{s\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; iu)] \quad (20)$$

We now make use of the Dyson-type equation that relates the interacting to the noninteracting response function^{18,19}:

$$\begin{aligned} \chi_{\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') &= \chi_{s\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') \\ &+ \sum_{\nu\nu'} \int d^3x d^3x' d\tau d\tau' \\ &\times \chi_{s\sigma\nu}(\mathbf{r}t, \mathbf{x}\tau) [w(\mathbf{x}, \mathbf{x}') \delta(\tau - \tau') \\ &+ f_{xc\ \nu\nu'}(\mathbf{x}\tau, \mathbf{x}'\tau')] \chi_{\nu'\sigma'}(\mathbf{x}'\tau', \mathbf{r}'t') \end{aligned} \quad (21)$$

Here, the xc kernel, $f_{xc\ \sigma\sigma'}$, is the functional derivative of the time-dependent xc potential:

$$f_{xc\ \sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{xc\ \sigma} [n_\uparrow, n_\downarrow](\mathbf{r}t)}{\delta n_{\sigma'}(\mathbf{r}'t')} \quad (22)$$

Transforming eq. (21) to the frequency domain, writing it for an arbitrary coupling constant, λ , and inserting it into eq. (20), leads to the exact formula:

$$\begin{aligned} E_c &= -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int d^3r d^3r' d^3x d^3x' w(\mathbf{r}, \mathbf{r}') \int_0^\infty du \\ &\sum_{\nu\nu'\sigma\sigma'} \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{x}; iu) \\ &\times [\lambda w(\mathbf{x}, \mathbf{x}') + f_{xc\ \nu\nu'}^{(\lambda)}(\mathbf{x}, \mathbf{x}'; iu)] \chi_{\nu'\sigma'}^{(\lambda)}(\mathbf{x}', \mathbf{r}'; iu) \end{aligned} \quad (23)$$

The noninteracting response function appearing in eq. (23) can be expressed in terms of the occupied

and unoccupied KS spin orbitals:

$$\begin{aligned} \chi_{s\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) &= \frac{1}{\hbar} \delta_{\sigma\sigma'} \sum_{jk} (f_{k\sigma} - f_{j\sigma}) \\ &\times \frac{\varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}')}{\omega - \omega_{j\sigma, k\sigma} + i\eta} \end{aligned} \quad (24)$$

$\omega_{j\sigma, k\sigma}$ is the frequency difference between the orbitals $\varphi_{j\sigma}$ and $\varphi_{k\sigma}$.

In this work, we do not try to solve the Dyson-type equation for the response function in a self-consistent manner. Rather, we employ approximations for $f_{xc}^{(\lambda)}$ and $\chi^{(\lambda)}$ on the right-hand side of eq. (23). They should be simple enough to allow some analytical integrations, so that we obtain a useful expression for the correlation energy. There are two exact properties of the response function that are helpful for constructing approximations⁸:

$$1. \text{ Charge conservation: } \int d^3r \sum_{\sigma} \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) = 0 \quad (25)$$

$$2. \text{ Reciprocity: } \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; i\omega) = \chi_{\sigma'\sigma}(\mathbf{r}', \mathbf{r}; -i\omega) \quad (26)$$

We examine the vdW behavior of the approximate functionals in the following way: We apply them to a system of two nonoverlapping subsystems A and B at a distance R . For large R , the total correlation energy consists of a constant part (the correlation energies of the isolated subsystems) plus a vdW part, which should asymptotically behave like:

$$E_{\text{vdW}} \simeq -\frac{C_6}{R^6} \quad \text{for } R \rightarrow \infty \quad (27)$$

where we have used the vdW coefficient, C_6 . Although none of the commonly used functionals produces the R^{-6} dependence at all, our approximations will, enabling us to calculate vdW coefficients from them.

APPROXIMATIONS

For the xc kernel, there exists a simple orbital-dependent formula, which was introduced by Pe-

tersilka, Gossmann, and Gross (PGG)^{19,20}:

$$f_{xc}^{(\lambda)}(\mathbf{r}, \mathbf{r}'; \omega) = -\lambda \delta_{\sigma\sigma'} w(\mathbf{r}, \mathbf{r}') \times \frac{|\sum_k f_{k\sigma} \varphi_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}')|^2}{n_{\sigma}(\mathbf{r}) n_{\sigma'}(\mathbf{r}')} \quad (28)$$

It is based on the time-dependent optimized effective potential method in the exchange-only approximation. Therefore, it is proportional to the coupling constant. Within this approximation the xc kernel does not depend on frequency. In what follows, we drop the frequency argument. We note that eq. (28), if inserted in eq. (23), leads to a self-interaction-free correlation energy functional; that is, E_c reduces to zero in the limit of one single particle.

For the response function, we test several approximations. First, we insert:

$$\chi_{\sigma\sigma'}^{(\lambda)} \simeq \chi_{s\sigma\sigma'} \quad (29)$$

on the right-hand side of eq. (23); that is, we use the noninteracting density response. Integrating over λ and u yields:

$$E_c^{\chi_s} = -\frac{1}{2\hbar} \sum_{\substack{jkmn \\ \sigma\sigma'}} f_{jk\sigma} f_{mn\sigma'} \int d^3r d^3r' d^3x d^3x' w(\mathbf{r}, \mathbf{r}') \times f_{hxc\sigma\sigma'}(\mathbf{x}, \mathbf{x}') \frac{M_{jk\sigma}(\mathbf{r}, \mathbf{x}) M_{mn\sigma'}(\mathbf{x}', \mathbf{r}')}{\omega_{j\sigma, k\sigma} + \omega_{m\sigma', n\sigma'}} \quad (30)$$

where:

$$f_{jk\sigma} = f_{k\sigma} (1 - f_{j\sigma}) \quad (31)$$

$$f_{hxc\sigma\sigma'}(\mathbf{x}, \mathbf{x}') = w(\mathbf{x}, \mathbf{x}') + f_{xc\sigma\sigma'}(\mathbf{x}, \mathbf{x}') \quad (32)$$

and:

$$M_{jk\sigma}(\mathbf{r}, \mathbf{x}) = \varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \varphi_{k\sigma}(\mathbf{x}) \varphi_{j\sigma}^*(\mathbf{x}) \quad (33)$$

The indices k and n label the occupied orbitals, and j and m label the unoccupied ones. Through a multipole expansion of the vdW part of eq. (30) we find the vdW coefficient for the interaction of two nonoverlapping subsystems A and B:

$$C_6^{\chi_s} = \frac{e^4}{\hbar} \sum_{i=1}^3 (1 + 3\delta_{3i}) \sum_{\substack{jkmn \\ \sigma\sigma'}} f_{jk\sigma} f_{mn\sigma'} \times \frac{|\langle k\sigma | r_i | j\sigma \rangle^{(A)}|^2 |\langle n\sigma' | r_i | m\sigma' \rangle^{(B)}|^2}{\omega_{j\sigma, k\sigma} + \omega_{m\sigma', n\sigma'}} \quad (34)$$

This involves dipole-operator matrix elements of the isolated subsystems.

Eq. (30) is similar to second-order perturbation theory. This gives rise to the problem that it will diverge if it is applied to the uniform electron gas. Nevertheless, we expect reasonable results for finite systems.

If we want to describe bulk metals, a different approach is necessary. For simplicity, we will restrict ourselves to spin-saturated systems in the following; that is:

$$n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) \quad (35)$$

$$\varphi_{j\uparrow}(\mathbf{r}) = \varphi_{j\downarrow}(\mathbf{r}) =: \varphi_j(\mathbf{r}) \quad (36)$$

$$\omega_{j\uparrow, k\uparrow} = \omega_{j\downarrow, k\downarrow} =: \omega_{jk} \quad (37)$$

$$M_{jk\uparrow}(\mathbf{r}, \mathbf{r}') = M_{jk\downarrow}(\mathbf{r}, \mathbf{r}') =: M_{jk}(\mathbf{r}, \mathbf{r}') \quad (38)$$

$$f_{j\uparrow} = f_{j\downarrow} =: f_j \quad (39)$$

$$f_{xc}(\mathbf{r}, \mathbf{r}') =: \frac{1}{4} \sum_{\sigma\sigma'} f_{xc\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \quad (40)$$

$$\chi(\mathbf{r}t, \mathbf{r}'t') =: \sum_{\sigma\sigma'} \chi_{\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') \quad (41)$$

A very simple ansatz is the hydrodynamic response function, which can be derived through a classical, pressure-free treatment of the uniform electron gas. In the homogeneous case it is given by:

$$\chi^{\text{hy}}(\mathbf{q}, \omega) = \frac{nq^2}{m(\omega^2 - \omega_p^2)} \quad (42)$$

with ω_p being the plasma frequency:

$$\omega_p^2 = \frac{4\pi ne^2}{m} \quad (43)$$

In ref. 8 it is suggested to generalize this to inhomogeneous systems by using it in a local sense and complying with the conditions of eqs. (25) and (26). This leads to:

$$\chi^{\text{hy}}(\mathbf{r}, \mathbf{r}'; \omega) = \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \frac{n(\mathbf{r})}{m(\omega^2 - \omega_p^2(\mathbf{r}))} \delta(\mathbf{r} - \mathbf{r}') \quad (44)$$

Obviously, to obtain the corresponding $\chi^{(\lambda)}$, we must replace ω_p^2 by $\lambda\omega_p^2$. Using this expression to evaluate the correlation energy from eq. (23), the integrations over λ and u can be done analytically, and the delta function in eq. (44) reduces the

number of spatial integrations. The final result is:

$$E_c^{\text{hy}} = \frac{1}{4\pi e^2} \int d^3r d^3x d^3x' [\nabla_r w(\mathbf{r}, \mathbf{x}')] \times [\nabla_{\mathbf{x}'} f_{\text{hxc}}(\mathbf{x}, \mathbf{x}')] \times \sum_{jk} f_k(1 - f_j) M_{jk}(\mathbf{r}, \mathbf{x}) f\left(\frac{\omega_{jk}}{\omega_p(\mathbf{x}')}\right) \quad (45)$$

where:

$$f(x) = 1 - 2x + 2x^2 \ln\left(1 + \frac{1}{x}\right) \quad (46)$$

Unfortunately, the correlation energy of the uniform electron gas is poorly described by this formula.²¹ The reason is that, for large wave numbers, the excitation frequencies of the electron gas are no longer given by the plasma frequency but rather by single-particle excitations. A so-called plasmon-pole model has been proposed to deal with this problem.²² Its basic idea is to assign just one excitation frequency, ω_q , to each wave number q . The plasmon-pole response function then reads:

$$\chi^{\text{pl}}(\mathbf{q}, \omega) = \frac{nq^2}{m(\omega^2 - \omega_q^2)} \quad (47)$$

The two most important conditions ω_q should satisfy are given by:

$$\omega_q \rightarrow \omega_p \quad \text{for } q \rightarrow 0 \quad (48)$$

$$\omega_q \simeq \frac{\hbar}{2m} q^2 \quad \text{for } q \rightarrow \infty \quad (49)$$

We use a very simple interpolation between both limits and include the λ -dependence:

$$\omega_q^{(\lambda)} = \omega_p^{(\lambda)} + \frac{\hbar}{2m} q^2 \quad (50)$$

The corresponding real-space response function of the homogeneous gas at imaginary frequencies is:

$$\chi^{(\lambda)}(\mathbf{r}, \mathbf{r}'; iu) = - \int \frac{d^3q}{(2\pi)^3} \frac{nq^2 e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{m[u^2 + (\omega_q^{(\lambda)})^2]} \quad (51)$$

In this expression the density is constant. The inhomogeneity in the density of the actual system of interest will be reintroduced later. Performing the integrations over u and \mathbf{q} in the correlation

energy formula leads to:

$$E_c = \frac{1}{4\pi e^2} \int d^3r d^3r' d^3x d^3x' \sum_{jk} f_k(1 - f_j) \times [\nabla_r w(\mathbf{r}, \mathbf{r}')] [\nabla_{\mathbf{x}'} f_{\text{hxc}}(\mathbf{x}, \mathbf{x}')] \times M_{jk}(\mathbf{r}, \mathbf{x}) \xi(\mathbf{x}' - \mathbf{r}') \quad (52)$$

where:

$$\xi(\mathbf{r}) = \frac{2n}{\hbar \omega_{jk}} \frac{e^2}{r} \int_0^1 d\lambda \times \lambda \left[e^{-r\sqrt{(2m/\hbar)\omega_p^{(\lambda)}}} - e^{-r\sqrt{(2m/\hbar)(\omega_p^{(\lambda)} + \omega_{jk})}} \right] \quad (53)$$

The integral in eq. (53) can be evaluated analytically. It is, however, more convenient to approximate the resulting, rather lengthy, expression by an exponential:

$$\xi(\mathbf{r}) \simeq ae^{-r/b} \quad (54)$$

We exploit the properties:

$$\left. \frac{d\xi(r)}{dr} \right|_{r=0} = - \left(\frac{2m\omega_p}{\hbar} \right)^2 \frac{1}{16\pi} \quad (55)$$

$$\int d^3r \xi(\mathbf{r}) = f\left(\frac{\omega_{jk}}{\omega_p}\right) \quad (56)$$

to determine a and b :

$$a = \left(\frac{2m\omega_p}{\hbar} \right)^{3/2} \frac{1}{16\pi} \left[2f\left(\frac{\omega_{jk}}{\omega_p}\right) \right]^{1/4} \quad (57)$$

$$b = \left(\frac{\hbar}{2m\omega_p} \right)^{1/2} \left[2f\left(\frac{\omega_{jk}}{\omega_p}\right) \right]^{1/4} \quad (58)$$

The function f appearing in these equations has been defined in eq. (46). With the simplification, eq. (54), we can do one spatial integration analytically, and we arrive at an expression similar to the hydrodynamic result:

$$E_c^{\text{pl}} = \frac{1}{4\pi e^2} \int d^3r d^3x d^3x' \sum_{jk} f_k(1 - f_j) \times [\nabla_r w_{\text{eff}}(\mathbf{r}, \mathbf{x}')] [\nabla_{\mathbf{x}'} f_{\text{hxc}}(\mathbf{x}, \mathbf{x}')] \times M_{jk}(\mathbf{r}, \mathbf{x}) f\left(\frac{\omega_{jk}}{\omega_p(\mathbf{x}')}\right) \quad (59)$$

which, in contrast to eq. (45), contains an “effective interaction”:

$$w_{\text{eff}}(\mathbf{r}, \mathbf{x}') = \frac{e^2}{|\mathbf{r} - \mathbf{x}'|} - e^2 \left(\frac{1}{2b(\mathbf{x}')} + \frac{1}{|\mathbf{r} - \mathbf{x}'|} \right) e^{-|\mathbf{r} - \mathbf{x}'|/b(\mathbf{x}')} \quad (60)$$

Here the inhomogeneity of the actual system of interest has been taken into account in the spirit of an LDA by evaluating $b(\mathbf{x}')$ from eq. (58) with the local plasma frequency $\omega_p(\mathbf{x}')$. For large distances, eq. (60) reduces to the Coulomb interaction. The short-range part, however, is cut off by the exponential. This is related to the fact that the difference between the hydrodynamic and the plasmon-pole response functions lies only in the high- q region. The vdW interaction is merely determined by the long-range behavior of w_{eff} . Therefore, both approximations yield exactly the same vdW coefficients, namely:

$$C_6^{\text{hy}} = \frac{e^2}{4\pi} \sum_{i=1}^3 (1 + 3\delta_{3i}) \sum_{jk} f_k (1 - f_j) \times \left\{ \left| \langle k|r_i|j \rangle^{(A)} \right|^2 F_{jk}^{(B)} + \left| \langle k|r_i|j \rangle^{(B)} \right|^2 F_{jk}^{(A)} \right\} \quad (61)$$

with:

$$F_{jk}^{(A)/(B)} = \int_{A/B} d^3r f \left(\frac{\omega_{jk}}{\omega_p(\mathbf{r})} \right) \quad (62)$$

It is a common feature of all our approximations that the xc kernel drops out in the multipole expansion leading to the vdW coefficient. Therefore, C_6 is not affected by the choice of f_{xc} .

Results

First, we take a brief look at the plasmon-pole calculation in the uniform electron gas. To separate the effect of the xc kernel, we first consider the correlation energy in the random phase approximation (RPA) which is obtained by setting $f_{\text{xc}} \equiv 0$. In Figure 1, we have plotted the RPA correlation energy per electron, ϵ_c^{RPA} , versus the Wigner–Seitz radius, r_s , which characterizes the density through

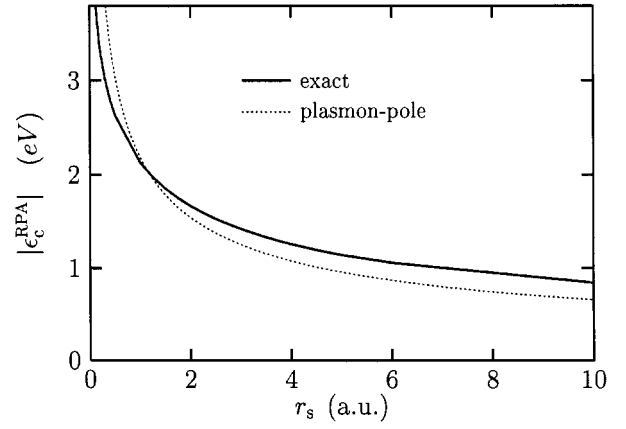


FIGURE 1. RPA correlation energy of the uniform electron gas.

the definition:

$$\frac{1}{n} = \frac{4\pi}{3} r_s^3 \quad (63)$$

Figure 2 shows the correction produced by the inclusion of the PGG xc kernel. In both cases, the agreement with the exact values is acceptable. For comparison, Figure 2 also shows the corrections produced by the local xc kernels:

$$f_{\text{xc}}^{\text{x-ALDA}}(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}') \frac{d^2}{dn^2} [n\epsilon_x(n)] \quad (64)$$

and:

$$f_{\text{xc}}^{\text{x-HFLDA}}(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}') \left[-\frac{4}{5} n^{2/3} \frac{d}{dn} \frac{\epsilon_x(n)}{n^{2/3}} \right] \quad (65)$$

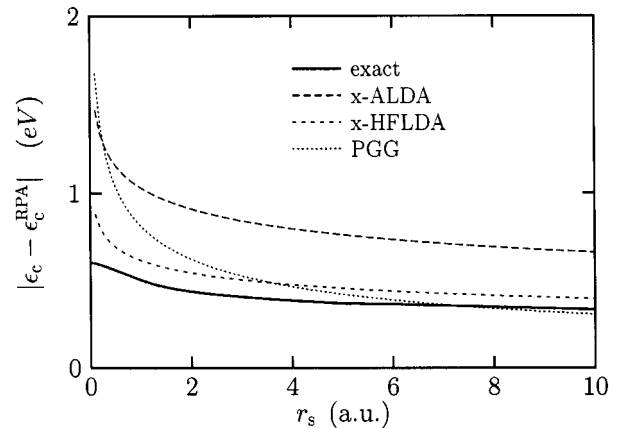


FIGURE 2. Correction to RPA in the uniform electron gas using different xc kernels. Exact values from Ceperley–Alder data (see refs. 23 and 24).

with:

$$\epsilon_x(n) = -\frac{3e^2}{4} \left(\frac{3n}{\pi} \right)^{1/3} \quad (66)$$

These are the exchange parts of the adiabatic local density approximation (ALDA) and the high-frequency local density approximation (HFLDA).¹⁸ We use only the exchange parts because they are proportional to the coupling constant, thus allowing the same analytical integrations that we did with the PGG approximation. It turns out that the x-ALDA corrections are too large by a factor of 2. On the other hand, the x-HFLDA kernel works surprisingly well.

Now we focus on the central issue, the vdW interaction. In the case of the plasmon-pole model we have evaluated the vdW coefficients, C_6 , for rare-gas atoms. For this purpose we have calculated numerical wave functions from existing xc functionals and inserted them into the C_6 functional. Recently, Andersson, Langreth, and Lundqvist (ALL) calculated C_6 with a different density functional method.⁷ However, their formula for the vdW energy, given by:

$$E_{\text{vdW}}^{\text{ALL}} = -\frac{3\hbar}{32\pi^2} \int_A d^3r \int_B d^3r' \times \frac{\omega_p(\mathbf{r})\omega_p(\mathbf{r}')}{\omega_p(\mathbf{r}) + \omega_p(\mathbf{r}')} \frac{1}{|\mathbf{r} - \mathbf{r}'|^6} \quad (67)$$

can be shown to originate from a hydrodynamic approximation also.⁸ Whereas, in the present work we have used the hydrodynamic response function in the exact expression for the total correlation energy, ALL substituted it into the Zaremba-Kohn formula,²⁵ which expresses the vdW energy ex-

actly in terms of response functions. When comparing our results with those of ALL we have to take into account that they have used a spatial cutoff that crucially alters the C_6 coefficients. They argue that the hydrodynamic approximation overestimates the density response in the outer region of an atom. Their cutoff criterion, which has already been used in an earlier work by Rapcewicz and Ashcroft,⁶ reads:

$$\frac{\nabla n}{6n} \geq \frac{\omega_p}{v_F} \quad (68)$$

where v_F is the local Fermi velocity. It skips those regions where the length scale for the change of the local Fermi wave vector is smaller than the electron screening length.

In Table I we show the vdW coefficients resulting from our approximation and the corresponding numbers from the ALL formula, eq. (67), with and without applying the cutoff, eq. (68). The wave functions stem from an exchange-only KLI calculation. Other functionals, such as the self-interaction corrected local density approximation (LDA-SIC),²⁴ give similar results, usually deviating from the x-only-KLI by about 5%. We find that, without using the cutoff, all numbers are much too large, but the present approximation performs better on average. The cutoff takes the ALL coefficients surprisingly close to the empirical numbers, whereas, in our case, the cutoff does not work as nicely.

Now we turn to the χ_s approximation. In Table II we compare the vdW coefficients with empirical numbers. Because this approach yields better coefficients than the plasmon-pole model, we have also included alkali atoms and hydrogen. While

TABLE I.
 vdW Coefficients C_6 from Various Hydrodynamic Approximations.^a

Atoms	ALL		Present		Empirical
	Without cutoff	With cutoff	Without cutoff	With cutoff	
He—He	42.7	1.95	6.58	2.68	1.458
Ne—Ne	77.5	6.84	21.3	10.9	6.383
Ar—Ar	328	63.4	219	139	64.30
Kr—Kr	525	123	422	285	129.6
Xe—Xe	914	264	937	669	285.9

^a The approximation due to Andersson, Langreth, and Lundqvist (ALL), eq. (67), is compared with the present formula, eq. (61), and empirical values. The calculation has been done with and without the cutoff, eq. (68). Wave functions from x-only-KLI. Empirical values from ref. 26. All numbers in atomic units.

TABLE II.
vdW Coefficients C_6 from the χ_s Approximation, Eq. (34).^a

Atoms	x-Only-KLI	CS-KLI	LDA-SIC-KLI	Empirical
He—He	1.664	1.639	1.594	1.458
He—Ne	3.490	3.424	3.495	3.029
Ne—Ne	7.447	7.284	7.761	6.383
Ar—Ar	128.5	124.4	133.2	64.30
Kr—Kr	282.4	271.3	290.0	129.6
Xe—Xe	730.7	697.1	734.6	285.9
Li—Li	1460	1313	1423	1390
Li—Na	1689	1453	1485	1450
Na—Na	1957	1614	1560	1510
K—K	6665	5265	4662	3890 ± 20
Rb—Rb	9624	7505	6347	4870 ± 70
H—He	3.022	2.995	2.948	2.82 ± 0.02
H—Ne	6.060	5.976	6.227	5.71 ± 0.07
H—Li	67.99	64.96	67.22	66.4 ± 0.5
H—Na	81.14	75.43	74.50	71.8 ± 0.3

^a Hydrogen wave functions were calculated from the exact potential, all other wave functions from x-only-KLI, Colle-Salvetti-KLI, or LDA-SIC-KLI potentials as indicated. Empirical values from ref. 26 and 27. Empirical values of the alkali atoms are accurate to three digits if no uncertainty is indicated. All numbers in atomic units.

the hydrogen wave functions have been obtained from the exact potential, we used x-only-KLI, Colle-Salvetti-KLI (CS-KLI)^{28, 29} and LDA-SIC-KLI wave functions for the other elements, as indicated. Indeed, eq. (34) is exact for the interaction of two hydrogen atoms, because hydrogen possesses only a single electron, the density response of which is given exactly by χ_s . So, it is not surprising that the calculated C_6 of 6.499 a.u. equals the empirical value²⁷ of (6.49 ± 0.02) a.u. in this case. As is obvious from the table, the results are good for the light atoms H, He, Li, Ne, and Na. For the heavier elements, however, the numbers become increasingly worse. Almost all numbers are bigger than the empirical values. We note that the rare-gas

values are less sensitive than the alkali values to what kind of wave functions are used. The vdW coefficient given by eq. (34) can also be obtained if one applies perturbation theory directly to the vdW energy; that is, if one uses $\chi \approx \chi_s$ in the Zaremba-Kohn formula.²⁵ This has been done by Görling and Levy, who have then used basis sets to evaluate C_6 leading to very similar results.³⁰ Table III shows atomic correlation energies computed from the χ_s approximation with the PGG xc kernel. These calculations have been done with x-only-KLI wave functions. In the case of He, Be, and Ne, Umrigar and Gonze have published practically exact numbers for the DFT correlation energy.^{31, 32} To judge the quality of the functional, we

TABLE III.
Atomic Correlation Energies from Various Approximations.^a

Atom	$E_c^{\chi_s}$	LDA	LDA-SIC-KLI	CS-KLI	PW91	Exact/empirical
He	-0.048	-0.111	-0.0582	-0.0416	-0.0450	-0.0421
Be	-0.13	-0.224	-0.1169	-0.0934	-0.0942	-0.0962
Ne	-0.41	-0.739	-0.4283	-0.3757	-0.3784	-0.394
Ar	-0.67	-1.423	-0.8330	-0.7435	-0.7687	-0.72

^a The χ_s approximation, eq. (30), using the PGG xc kernel, eq. (28), is compared with self-consistent DFT results and with exact DFT correlation energies for He, Be, and Ne^{31, 32} as defined by eq. (12) and the conventional quantum-chemical correlation energy for Ar³³ as defined in eq. (17). All numbers in hartrees.

TABLE IV.
Total Atomic Ground-State Energies from Various Approximations.^a

Atom	E^{χ_s}	LDA	LDA-SIC-KLI	CS-KLI	PW91	Exact/empirical
He	-2.910	-2.835	-2.920	-2.903	-2.900	-2.9037
Be	-14.71	-14.446	-14.695	-14.665	-14.648	-14.6674
Ne	-128.96	-128.230	-129.287	-128.920	-128.947	-128.939
Ar	-527.48	-525.940	-528.432	-527.553	-527.539	-527.604
$\bar{\Delta}_r$ (%)	0.14	1.19	0.29	0.016	0.070	

^a Total energies obtained from the χ_s approximation using the PGG xc kernel, eq. (28), are compared with self-consistent DFT results and exact/empirical values.^{3,34} $\bar{\Delta}_r$ denotes the mean relative deviation from the exact/empirical values. All energies in hartrees.

also compare with results of self-consistent DFT calculations using some established xc functionals. Finally, in Table IV, we compare total ground-state energies. Here, E^{χ_s} is the sum of the x-only-KLI total energy and the correlation energy, $E_c^{\chi_s}$ (Table III), whereas the other values are from self-consistent calculations as in Table III. The mean relative deviation from the exact/empirical numbers shows that our approximation is superior to the LDA and to the LDA-SIC. On the other hand, the orbital-dependent CS functional and the GGA of Perdew and Wang (PW91)³⁵ perform better in this context.

Conclusion

We have described an approach that allows the treatment of vdW interactions in DFT. We have presented several approximations of the correlation energy functional that include vdW energies. The numerical results show that our approximations need further improvement to give reliable results for arbitrary systems. Some aspects, however, are already described quite well, especially the vdW coefficients of light atoms as well as the total correlation energies of rare-gas atoms. The xc kernel of Petersilka, Gossmann, and Gross has proved to be very useful in the present context. The main progress is that, in contrast to previous work, we have calculated vdW energies and total correlation energies from one and the same functional.

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